Polymerization Studies of Unsaturated Derivatives of Beta-Nitrostyrene

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CHAPTER I

INTRODUCTION AND HISTORICAL NOTES

A. Literature Review

1. Preparation of Aldehyde Intermediates

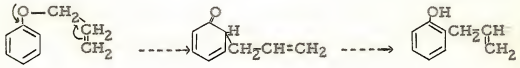
The methods which have most generally been used in the preparation of allyl aryl ethers, namely, refluxing of the phenol with allyl bromide and anhydrous potassium carbonate in acetone and higher boiling ketones such as methyl ethyl ketone, have been unsatisfactory for phenolic aldehydes, especially those which condense with ketones in the presence of potassium carbonate. Consequently, absolute ethanol has been substituted for the ketones with excellent results (13).

The rearrangement of allyl ethers of enols and phenols to C-allyl derivatives when heated to high temperatures was first observed by L. Claisen (14, 15) when he attempted to distill O-allylacetoacetate at atmospheric pressure in the presence of ammonium chloride and beta-naphthol allyl ether under twelve millimeters pressure. This rearrangement has been extended to include several substituents in the aromatic nucleus as well as a great number of heterocyclic nuclei (56). None of the substituents in the aromatic nucleus affect the rearrangement to any appreciable extent. The meta directing groups

do not hinder the reaction, and correspondingly, strong ortho-para directing groups do not favor it. Ester groups do not interfer with the rearrangement, but, if a free carboxyl or aldehyde group is ortho or para to the allyloxy group, it may be replaced by the allyl radical with evolution of carbon dioxide and carbon monoxide respectively (13).

With the exception of a very few cases such as derivatives of polyhydrobenzenes (3, 33, 43, 54), the migration of the allyl group has always been to the ortho position, when available, and has produced good yields. In the exceptions, this migration has been to the para position. If the ortho positions have been occupied, the migrating allyl group has occupied the para position. In the case where the two ortho and the para positions have been occupied, the compound undergoes decomposition or as mentioned above, replaces groups such as the carboxyl and aldehyde, but, never enters the meta position (13, 16).

The mechanism of the rearrangement is represented by the following illustration (17, 18, 19, 30, 59):



A study of several allyl ethers has shown that in no case where the rearrangement takes place to the ortho positions is the substituted

allyl group attached to the nucleus after rearrangement by the same carbon atom which was attached to the oxygen. The attachment has usually been by the gamma-carbon which involves inversion with a subsequent shift of the double bond of the allyl group from the beta, gamma-position to the alpha, beta-position. Exceptions are gamma-ethylallyl phenyl ether (30, 37) and gamma-propylallyl phenyl ether (38) where the delta-carbon attaches itself to the nucleus.

The rearrangement to the ortho-position has been classified as a first-order reaction (34, 35) and as was expected required neither acid nor base to catalyze it. The breaking of the carbon-oxygen bond and the attachment of the gamma-carbon to the ortho-position must be simultaneous. This step, rather than enolization of the hydrogen, must be the rate-determining step. The rearrangement has been shown to be intramolecular, since mixtures of allyl ethers yield none of the cross products which would result in an intermolecular reaction (31).

2. Preparation of β-Nitrostyrenes

Simon (52), in 1839, prepared and identified the first of many nitrostyrene derivatives when he nitrated the steam distillate of "storax oil," which was predominantly cinnamic acid, and obtained β-nitrostyrene.

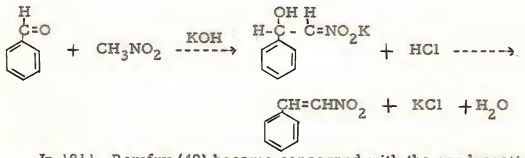
Until the later part of the nineteenth century, when Henry (27) prepared β-nitrostyrenes by condensation of the appropriate aromatic

aldehyde with nitromethane in the presence of zinc chloride at elevated temperatures, nitration of acids similar in structure to cinnamic acid was the only method used in preparing β-nitrostyrenes.

Priebs (46) and Posner (45) studied the method of Henry by preparing various β-nitrostyrenes. Priebs also studied the effect of alkali on the compounds he obtained and reported that amorphous products resulted which could not be identified. We assume on the basis of work done today that these unidentifiable materials are the polymers of the original β-nitrostyrenes. Meisenheimer (41) reported that sodium methylate when added to β-nitrostyrene entered the 1, 4-positions, forming a salt, but, fifty to eighty per cent of the β-nitrostyrene formed an amorphous solid. No further study of this was reported until Butler and Carter (10) polymerized several β-nitrostyrenes by the use of sodium methylate.

Thiele (57, 58) made additional studies on the condensation of aromatic aldehydes with nitromethane and found that an excess of alcoholic potassium hydroxide served exceptionally well as a condensing agent at a temperature of 0°C. In this condensation an intermediate salt is formed with the alkali which upon treatment with an excess of acid, usually hydrochloric, yields the β-nitrostyrene. Bouveault and Wahl (5) reported that the method of Thiele was not satisfactory in every case for the preparation of β-nitrostyrenes and used sodium

methoxide as the condensing agent, in place of alcoholic potassium hydroxide. The reaction equations involving a base are as follows:



In 1911, Remfry (49) became concerned with the condensation of aromatic aldehydes with nitromethane in the presence of alkali and, from reports of previous investigators, concluded that the character of the substituent groups on the aromatic nucleus had an effect on the subsequent condensation of the aldehydes. Even though he was unable to admit any generalization with regard to the condensation, his study gave some indication of the effect that certain groups exhibited in the various positions on the aromatic nucleus. He found that the hydroxyl group substituted in the para position, alone or in conjunction with other groups, inhibits this condensation. The free carboxyl groups also prevent condensation, but, upon esterification will not interfere.

Knoevenagel and Walter (36) and Hahn and Stiehl (26) observed that 4-hydroxy-3-methoxybenzaldehyde did not condense with nitromethane under Thiele's procedure, but, the condensation did take place in good yields with methylamine as the catalyst. Burton and Duffield (9) stated that the condensation of 4-hydroxybenzaldehyde with

nitromethane was best effected with methylamine or aniline as the catalyst, according to unpublished data obtained in 1934 by C. W. Shoppee, but gave no details. Hahn and Stiehl report no condensation of 4-hydroxybenzaldehyde with nitromethane by Thiele's method or by use of methylamine as catalyst, whereas, Schales and Graefe (51) using aniline as catalyst and heat obtained the desired product in good yield.

In the previously mentioned case of Knoevenagel and Walter, the time required for the reaction to go to completion was approximately one week. Worrall and Cohen (61) described a faster modification which also used a primary amine as a catalyst, but required a short heating period. Other methods are: addition of N_2O_4 to styrene (60), nitration of various phenyl ethylenes (1, 2, 32), use of ammonium acetate and glacial acetic acid as a catalyst (41), addition of nitrosyl chloride to styrenes (44), addition of nitryl chloride to styrenes (55), and use of nitro alcohols heated with phthalic anhydride (8).

The preparation of β-nitrostyrenes has continued for the past twenty years not only for themselves alone, but, as intermediates in the preparation of various amines and oximes either by electrolytic reduction (53), or catalytic hydrogenation (47, 48, 64). Worrall has studied the 1, 4 addition of various basic organic compounds particularly amino and hydroazino bases (62, 63, 64, 65, 66). β-Nitrostyrenes have recently been checked and found in many instances to be

effective in combating insects (6, 40), fungi (4, 6, 40), mold (10) and bacteria (4, 20, 40, 51).

3. Alkali Polymerization of β-Nitrostyrenes

The effect of alkali on β-nitrostyrenes was noted by Priebs when he reported that amorphous products resulted which could not be identified (46). Meisenheimer (41) also reported that when sodium methylate was added to β-nitrostyrenes, fifty to eighty per cent formed an amorphous solid. No further study of this was reported until Butler and Carter (10) reported that eleven β-nitrostyrenes were polymerized by using catalytic amounts of sodium ethylate in absolute ethanol. All of the polymers were either amorphous solids or very viscous gums. Only the viscous gums were soluble to varying extents in acetone and alcohol. On the basis of this latter work it is reasonable that the unidentifiable materials of Priebs and Meisenheimer were the polymers of the original β-nitrostyrenes.

4. Polymerization of Vinyl Substituted Ethers

The earliest polymerization of ethers containing a vinyl group or groups was carried out in the presence of inorganic polymerizing agents such as $SnCl_2$, $SnCl_4$, $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_3$, and $ZnCl_2$ (21). The ethers used included several alkyl vinyl ethers, aryl vinyl ethers, and the mono- and di-vinyl ethers of di- and tri-ethylene

glycols and polyglycols.

Vinyl ethers of formula R'R"CR"'OR, in which R was aliphatic, aromatic, or hydroaromatic radical and R', R", and R"' were hydrogen atoms or aliphatic residues, were polymerized by bringing them, singly or in a mixture, into contact with the inorganic agents listed above and in addition BF_3, HBF_4, $SiCl_4$, $KHSO_4$, alum, or practically anhydrous H_2SO_4, H_3PO_4, HCl, or HF (22). The products may be employed in coating and adhesive purposes, as substitutes for oils in oil-filled sub-oil or submarine cables, as substitutes for polishing waxes, as intermediate layers in laminated glass and as softening and plastifying agents for India rubber and rubber-like polymerization products of diolefins or for masses from polymerized styrene. Ethers of the general formula $R^1R^2C{:}C(OR)R^3$ in which R denotes an aliphatic, aromatic or hydroaromatic hydrocarbon radical or a radical of the glycols or polyglycols or their monovinyl, monovinyl alkyl, monoalkyl, monocycloalkyl or monoaryl ethers, and R^1, R^2 and R^3 denote hydrogen atoms or alkyl radicals, gave, when polymerized in the presence of the above agents, products with similar properties and uses (50).

Alkyl and aryl vinyl ethers have been found to undergo violent polymerization upon addition of iodine (12). Considerable differences in polymerizability were discussed, and the aryl ether was found to be

the least sensitive to its action. A closed ring chain structure with the structural units arranged in regular order and joined by normal single bonds was proposed for the polymer.

Rubber-like products were obtained when vinyl isobutyl ether was polymerized below 10°C. in the presence of a small portion of volatile halide such as BF_3 (23).

Sulfur dioxide was used as a polymerizing agent (with or without conjoint use of other polymerizing agents such as $AlCl_3$ or BF_3) at a temperature of -10°C. or lower with ethers such as vinyl butyl ether, vinyl ethyl ether, the vinyl ether of N-hydroxyethyl-m-toluidine or glycerol formaldehyde acetal vinyl ether (24).

Vinyl butyl ether, vinyl ethyl ether, and vinyl ethers of N-hydroxyethyl-m-toluidine, N-hydroxyethyl aniline, N-hydroxyethyl-m-chloroaniline, 8-hydroxy-quinoline, ethanolamine, glycerol formaldehyde acetal, and the corresponding acetals from acetaldehyde, benzaldehyde and acetone, or mixtures of these ethers were polymerized by treatment with SO_2 with or without solvents (25). The polymer of N-hydroxyethyl-m-toluidine may be coupled with diazo solutions to give dyes of high molecular weight.

Ethers containing both vinyl and allyl groups have been prepared and polymerized. It was found that ethers of this type possessed a combination of properties of particular value in coating compounds (28).

These ethers were easily polymerized in solution in an organic solvent in contact with a catalyst such as $FeCl_3$ or $SnCl_4$. Paul, Roy, Fluchaire and Collardeau (42) and Butler and Nash (11) accomplished polymerization of ethers of the type described in two steps. In the case of Paul, Roy, Fluchaire and Collardeau, polymerization of the vinyl group in vinyl allyl ether was carried out at temperatures less than 25°C. using toluene as the solvent and $BF_3(C_2H_5)_2O$ as the catalyst. Butler and Nash reported that vinyl allyl or substituted allyl ethers of ethylene glycol in toluene at -70°C. was polymerized using $BF_3(C_2H_5)_2O$ as the catalyst. In both cases linear polymers were obtained. In the second step of this polymerization, Paul, Roy, Fluchaire and Collardeau used benzoyl peroxide, below 100°C. in the absence of air, to catalyze the reaction thus producing a hard and breakable substance, insoluble in organic solvents and dilute acid, but, soluble in concentrated HNO_3 and H_2SO_4. Butler and Nash using benzoyl peroxide at 65°C., completed the polymerization of the linear polymers they obtained from ethylene glycol vinyl allyl ether and ethylene glycol vinyl crotyl ether. The polymers obtained in this second step were insoluble in organic solvents and showed no signs of softening when heated thus suggesting cross-linked polymers.

B. Statement of the Problem

For many purposes it is important to impart to a polymer in its final state, as film, coating or moulded article, a high resistance against solvents and swelling agents and a considerable degree of surface hardness. The presence of two or more functional groups possessing the same degree of reactivity toward polymerization catalysts result in the formation of cross-linked or thermoset polymers. This is a distinct disadvantage in many cases for the uses outlined above.

The desired situation is to be able to carry out the polymerization as a two-step process. This would involve a process of controlled cross-linking, in the sense that in the first phase of polymerization, long linear chain molecules are being produced, which are soluble, plasticisable and thermoplastic. The cross-linking of such molecules is supposed to set in after the main form-giving process is completed.

The feasibility of such a two-step process has been demonstrated; for example, Butler and Nash (11) prepared diethers of ethylene glycol in which one group was the vinyl radical, the other group was the allyl or substituted allyl radical, and Paul, Roy, Fluchaire and Collardeau (42) prepared vinyl allyl ether. In both cases cited, the linear polymers were formed through the vinyl groups using BF_3 as the catalyst and cross-linked by a peroxide catalyst through the allyl group.

As has been noted in the previous discussion (10), β-nitrostyrene derivatives when treated with alkali such as sodium ethylate, form amorphous materials, and vinyl and allyl groups show differences in reactivity toward polymerization catalysts (11, 42), that monomeric compounds containing any combination of these functional groups should be able theoretically to lend themselves under proper conditions to such a two-step process. Consequently, the preparation, identification, and polymerization of monomers containing the vinyl and β-nitrostyrene radicals, the allyloxy and β-nitrostyrene radicals, and the allyl and β-nitrostyrene radicals has been pursued.

C. Source and Purification of Reactants

Vinyl-β-chloroethyl ether was obtained from Carbide and Carbon Chemical Corporation and was redistilled and the fraction boiling between 107-110°C. was recovered for use. 2-Hydroxybenzaldehyde and 3-hydroxybenzaldehyde were obtained from Eastman Organic Chemicals and Eastman Kodak Company respectively, and were used without further purification. Allyl bromide and 4-hydroxybenzaldehyde were obtained from the Matheson Company, Incorporated, and used without further purification. 3-Methoxy-4-hydroxybenzaldehyde was obtained from the Monsanto Chemical Company and was used without further purification. Benzoyl peroxide was obtained from the Lucidol Division, Novadel-Agene Corporation. Boron trifluoride was obtained in the form of the diethyl ether complex from General Chemical Company.

CHAPTER II

PREPARATION OF ALDEHYDE INTERMEDIATES

A. General Discussion

The general method found to be the most satisfactory for preparing the aldehydes was as follows: usually one-half mole of the appropriate phenolic aldehyde was dissolved in normal sodium hydroxide solution and placed in a flask equipped with mechanical stirrer, condenser, addition funnel, and thermometer. An equal molar quantity of allyl bromide was then added dropwise while the solution was heated on a steam bath. Heating was continued from four to eight hours after the addition of the bromide. The reaction mixture was cooled and extracted with benzene. The benzene was removed by distillation, using the steam bath as a source of heat. The residue was distilled under reduced pressure.

When vinyl 2-chloroethyl ether was to be condensed with the phenol in question, heat was applied for twenty-four hours, otherwise, the general procedure as above applies.

In order to rearrange the substituted ally phenyl ethers a flask was connected to an air condenser fitted with a thermometer. Heat was applied, usually by an electric mantle. The time necessary to

form the rearranged product was fifteen minutes to five hours and the temperature most generally used was 220-230°C.

The phenols formed by the rearrangement were dissolved in normal sodium hydroxide solution and were placed in a suitable flask equipped with mechanical stirrer, addition funnel, thermometer, and condenser. Dimethylsulfate was then added dropwise while holding the temperature below 40°C. Heat was applied for four to eight hours after the addition had been completed. Upon cooling, the mixture was extracted with benzene and distilled. The benzene was removed by distillation on a steam bath and the residue distilled under reduced pressure.

Temperatures recorded for the boiling and melting points are uncorrected. Pressures above five millimeters were measured with a Zimmerli gauge while those below five millimeters were measured with a McLeod gauge.

The refractive indexes were determined by means of an Abbe refractometer at 25°C. White light was the source of illumination.

The specific gravities were determined at 25°C. with a calibrated two milliliter specific gravity bottle. Freshly distilled portions of the compounds were used in both the density and refractive index determinations.

The carbon-hydrogen content of the aldehydes was found by use

of a semi-micro combustion train following the method of Pregl. Cerium oxide on pumice was used as the catalyst and Ascarite and Dehydrite as the adsorbing agents.

The properties, analyses, and yields of these new aldehydes are summarized in Tables I and II. Individual details not covered in this general discussion are found in the experimental part of this section.

TABLE I

PHYSICAL CONSTANTS OF NEW ALDEHYDES

Name	n_D^{25}	d_4^{25}	MR_D Calcd.	MR_D Found	b.p. °C/mm	m.p. °C	% Yield
3-Allyl-4-methoxybenzaldehyde	1.5648	1.0686	50.58	50.37	110-12/2		29.06
3-Allyloxybenzaldehyde	1.5497	1.0777	45.97	47.92	71-4/0.3-0.5		52.35
3,4-Dimethoxy-5-allylbenzaldehyde	1.5577	1.1134	56.85	59.49	112-16/1.5		61.01
2-(2-Vinyloxy)ethoxybenzaldehyde	1.5448	1.1146	52.23	54.41	120-4/0.5		31.53
3-(2-Vinyloxy)ethoxybenzaldehyde	1.5452	1.1178	52.23	54.25	106-9/0.3		42.46
4-(2-Vinyloxy)ethoxybenzaldehyde	1.5608	1.1195	52.23	55.58	115/0.1	37-8	18.70
3-Methoxy-4-(2-vinyloxy) ethoxybenzaldehyde						77-8	21.69

TABLE II

ANALYSES OF NEW ALDEHYDES

Compound	Formula	Calcd. % C	Calcd. % H	Found % C	Found % H
3-Allyl-4-methoxybenzaldehyde	$C_{11}H_{12}O_2$	74.97	6.89	74.64	6.94
3-Allyloxybenzaldehyde	$C_{10}H_{10}O_2$	74.05	6.21	73.97	6.31
3,4-Dimethoxy-5-allylbenzaldehyde	$C_{12}H_{14}O_3$	69.88	6.84	69.59	7.14
2-(2-Vinyloxy) ethoxybenzaldehyde	$C_{11}H_{12}O_3$	68.73	6.29	68.43	6.25
3-(2-Vinyloxy)ethoxybenzaldehyde	$C_{11}H_{12}O_3$	68.73	6.29	68.57	6.47
4-(2-Vinyloxy)ethoxybenzaldehyde	$C_{11}H_{12}O_3$	68.73	6.29	68.95	6.38
3-Methoxy-4-(2-vinyloxy) ethoxybenzaldehyde	$C_{12}H_{14}O_4$	64.85	6.35	64.99	6.28

B. Experimental

1. Preparation of 3-Allyl-4-methoxybenzaldehyde

a. Preparation of 4-allyloxybenzaldehyde: Sixty-one and one-tenth grams (five-tenths mole) of 4-hydroxybenzaldehyde, sixty and five-tenths grams (five-tenths mole) of allyl bromide, and sixty-nine and one-tenth grams (five-tenths mole) of potassium carbonate were placed in a five hundred milliliter flask containing three hundred milliliters of ninety-five per cent ethanol. The flask was fitted with a water-cooled reflux condenser, mechanical stirrer, and thermometer. The mixture was heated to reflux with stirring for six hours and then allowed to cool to room temperature. The salt which formed was removed by filtration and the ethanol removed by distillation. The residue which remained after removal of the ethanol was distilled under reduced pressure. The boiling point was 140-42°C. at ten millimeters. The yield was fifty-five and nine-tenths grams. The known boiling point was 142°C. at 10 millimeters.

b. Preparation of 3-allyl-4-methoxybenzaldehyde from 4-allyloxybenzaldehyde: Forty grams of the 4-allyloxybenzaldehyde prepared as in (a) was heated, in a three hundred milliliter flask equipped with an air cooled condenser and thermometer, at 260-70°C. for two hours. Upon cooling, the dark, viscous material was dissolved in two hundred and fifty milliliters of normal sodium hydroxide solution

and placed in a five hundred milliliter flask equipped with mechanical stirrer, thermometer, addition funnel, and water-cooled condenser. Thirty-one and five-tenths grams of dimethyl sulfate was added dropwise while the temperature was maintained below 40°C. After the addition had been completed the resulting mixture was heated for eight hours on a steam bath. Upon cooling the mixture was made basic with sodium hydroxide solution and extracted with three fifty-milliliter portions of benzene. The benzene was removed by distillation on a steam bath and the residue distilled under reduced pressure. The yield was twelve and eight-tenths grams.

Physical Constants: D_4^{25} 1.0686; n_D^{25} 1.5648; b.p. 112-15° at 2-3 millimeters; MR_D calculated 50.58; MR_D found 50.37.

2. Preparation of 3-Allyloxybenzaldehyde

Thirty grams (twenty-five-hundredths mole) of 3-hydroxybenzaldehyde was dissolved in two hundred and fifty milliliters of normal sodium hydroxide solution and placed in a five hundred milliliter flask equipped with mechanical stirrer, thermometer, and water-cooled condenser. Thirty grams of allyl bromide was added dropwise with stirring while the solution was heated on a steam bath. The resulting mixture was refluxed for eight hours, and upon cooling was found to consist of two layers. The dark, oily layer was collected by means of a separatory funnel and the remaining solution extracted with

twenty-five milliliters of benzene. The oily material and the benzene extract were combined and the benzene removed by distillation on a steam bath. The residue was distilled under reduced pressure. The yield was forty-eight and nine-tenths grams.

Physical Constants: D_4^{25} 1.0777; n_D^{25} 1.5497; b.p. 71-4° at 0.3-0.5 millimeters; MR_D calculated 45.97; MR_D found 47.92 .

3. Preparation of 3,4-Dimethoxy-5-allylbenzaldehyde

a. Preparation of 3-methoxy-4-allyloxybenzaldehyde: One hundred and fifty-two grams (one mole) of 3-methoxy-4-hydroxybenzaldehyde and one gram of Santomerse, a product of Monsanto Chemical Company, were dissolved in a solution of sodium hydroxide composed of forty grams of sodium hydroxide in four hundred and sixty milliliters of water. This solution was placed in a flask equipped with mechanical stirrer, thermometer, addition funnel and condenser. One hundred and twenty-two grams (one mole) of allyl bromide was added dropwise while the soltuion was heated on a steam bath. The resulting mixture was heated with stirring for six additional hours upon completion of the addition of the allyl bromide. Upon cooling the layers were separated and the organic material distilled under reduced pressure. The yield was one hundred and sixty-seven grams. The boiling point was 135-41° at 1.5 to 2 millimeters.

b. Preparation of 3,4-dimethoxy-5-allylbenzaldehyde from 3-methoxy-4-allyloxybenzaldehyde: Eighty-two grams (forty-three-hundredths mole) of 3-methoxy-4-allyloxybenzaldehyde was divided into two portions and placed in flasks equipped with air cooled condensers and thermometers. Each flask was heated at 220-30°C. for fifteen minutes. Upon cooling, the rearranged products were collected and dissolved in four hundred and thirty milliliters of normal sodium hydroxide solution. This solution was placed in a liter flask equipped with mechanical stirrer, addition funnel, water-cooled condenser, and thermometer. Fifty-four and two-tenths grams (forty-three-hundredths mole) of methyl sulfate was added dropwise with stirring while the temperature was maintained below 40°C. Upon completion of the addition, the mixture was heated on a steam bath for twenty-four hours. The mixture was then cooled and made basic by adding an excess of sodium hydroxide solution and extracted with two fifty-milliliter portions of benzene. The benzene was removed by distillation on a steam bath and the residue distilled under reduced pressure. The yield was fifty-three and two-tenths grams.

Physical Constants: D_4^{25} 1.1134; n_D^{25} 1.5577; b.p. 112-16° at 1.5 millimeters; MR_D calculated 56.85; MR_D found 59.49.

4. Preparation of 2-(2-Vinyloxy)ethoxybenzaldehyde

Sixty-one and one-tenth grams (five-tenths mole) of

2-hydroxybenzaldehyde was dissolved in five hundred milliliters of normal sodium hydroxide solution and placed in a liter flask equipped with mechanical stirrer, water-cooled condenser, addition funnel and thermometer. Fifty-three grams (five-tenths mole) of vinyl 2-chloroethyl ether was added dropwise with stirring while the mixture heated on a steam bath. The heating was continued for twenty-four hours after the addition had been completed and upon cooling the mixture was extracted with three fifty-milliliter portions of benzene. The benzene was removed by distillation when heated on a steam bath and the residue distilled under reduced pressure. The yield was thirty and three-tenths grams.

Physical Constants: D_4^{25} 1.1195; n_D^{25} 1.5448; b.p. 120-4° at 0.5 millimeters; MR_D calculated 52.23; MR_D found 54.41.

5. Preparation of 3-(2-Vinyloxy)ethoxybenzaldehyde

Thirty grams (twenty-five-hundredths mole) of 3-hydroxybenzaldehyde was dissolved in two hundred and fifty milliliters of normal sodium hydroxide solution and placed in a five hundred milliliter flask equipped with mechanical stirrer, water cooled condenser, addition funnel, and thermometer. Twenty-six and five-tenths grams (twenty-five-hundredths mole) of vinyl 2-chloroethyl ether was added dropwise with stirring while heated on a steam bath. Heating of the mixture was continued for twenty-four hours after the addition had

been completed and upon cooling was extracted with three fifty-milliliter portions of benzene. The benzene was removed by distillation when heated on a steam bath and the residue distilled under reduced pressure. The yield was twenty and four-tenths grams.

Physical Constants: D_4^{25} 1.1178; n_D^{25} 1.5452; b.p. 106-9° at 0.3 millimeters; MR_D calculated 52.23; MR_D found 54.25.

6. Preparation of 4-(2-Vinyloxy)ethoxybenzaldehyde

Sixty-one and one-tenth grams (five-tenths mole) of 4-hydroxybenzaldehyde was dissolved in five hundred milliliters of normal sodium hydroxide solution and placed in a liter flask equipped with mechanical stirrer, water-cooled condenser, addition funnel and thermometer. Fifty-three grams (five-tenths mole) of vinyl 2-chloroethyl ether was added dropwise with stirring while the mixture was heated on a steam bath. The heating of the mixture was continued for twenty-four hours after the addition had been completed, and upon cooling the mixture was extracted with two fifty-milliliter portions of benzene. The benzene was removed by distillation when heated on a steam bath and the residue distilled under reduced pressure. The yield was eighteen grams. The liquid solidified upon standing at room temperature.

Physical Constants: D_4^{25} 1.1195; n_D^{25} 1.5608; b.p. 120-5° at 1.5 millimeters; MR_D calculated 52.23; MR_D found 55.58; m.p.

37-8°C.

7. Preparation of 3-Methoxy-4-(2-Vinyloxy)ethoxy-benzaldehyde

One hundred fifty-two and two-tenths grams (one mole) of 3-methoxy-4-hydroxybenzaldehyde was dissolved in five hundred milliliters of two normal sodium hydroxide solution and placed in a liter flask equipped with mechanical stirrer, water-cooled condenser, addition funnel and thermometer. One hundred and six grams (one mole) of vinyl 2-chloroethyl ether was added dropwise with stirring while the mixture was heated on a steam bath. The heating was continued for twenty-four hours after the addition had been completed and upon cooling was found to contain solid material. The solid was collected by filtration and recrystallized from ethanol. The yield was forty-eight and two-tenths grams.

Physical Constant: m.p. 77-8°C.

8. Preparation of 2-Methoxy-3-allylbenzaldehyde

a. Preparation of 2-allyloxybenzaldehyde: Two hundred and forty-four grams (two moles) of 2-hydroxybenzaldehyde and two grams of Santomerse D were dissolved in a solution of sodium hydroxide composed of eighty grams of sodium hydroxide in nine hundred and twenty milliliters of water. This solution was placed in a flask

equipped with mechanical stirrer, thermometer, addition funnel, and condenser. Two hundred and forty-four grams (two moles) of allyl bromide was added dropwise while the solution was heated on a steam bath. The resulting mixture was heated with stirring for six additional hours upon completion of the addition of the allyl bromide. Upon cooling, the layers were separated and the material distilled under reduced pressure. The yield was two hundred forty-four grams. The boiling point was 97-102° at 2-3 millimeters.

b. Preparation of 2-methoxy-3-allylbenzaldehyde from 2-allyloxybenzaldehyde: Eighty-one and one-tenth grams (five-tenths mole) of 2-allyloxybenzaldehyde was placed in a three hundred milliliter flask equipped with an air cooled condenser and thermometer. The contents of the flask were heated to 220-230°C. for five hours. A sharp increase in the rate of rise of the temperature was noted at 210-20°. The rearranged material was dissolved in five hundred milliliters of normal sodium hydroxide solution and placed in a liter flask equipped with mechanical stirrer, addition funnel, water-cooled condenser, and thermometer. Sixty-three and one-tenth grams (five-tenths mole) of dimethyl sulfate was added dropwise with stirring while the temperature was maintained below 40°C. Upon completion of the addition, the mixture was heated on a steam bath for four hours. The mixture was then cooled and made basic by adding an excess of sodium hydroxide

solution and extracted with three fifty-milliliter portions of benzene. The benzene was removed by distillation on a steam bath and the residue distilled under reduced pressure. The yield was twenty-four grams. The boiling point was 121-5° at 7-8 millimeters. The known boiling point was 128° at 9 millimeters.

CHAPTER III

PREPARATION OF β-NITROSTYRENES

A. General Discussion

The general method found to be the most satisfactory for the preparation of the β-nitrostyrenes was as follows: usually five-hundredths mole of the appropriate aldehyde and an equal molar quantity of nitromethane were dissolved in methanol and placed in a flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Sodium hydroxide equal in molar quantity to the aldehyde used was dissolved in water, cooled to 10°C., and added dropwise to the solution of aldehyde and nitromethane. The period of reaction after the addition of the base varied from fifteen minutes to six hours. The reaction mixture was then poured into ice water and added at a fast drop-rate to an excess of hydrochloric acid solution. Usually, a yellow, bulky precipitate formed which was recrystallized from methanol or ethanol. In two cases an oil separated when the reaction mixture was added to the excess acid. The oil was subjected to distillation under reduced pressure.

Temperatures recorded for the boiling and melting points are uncorrected. Pressures were measured by a McLeod gauge.

The refractive indexes were determined by means of an Abbe refractometer at 25°C. White light was the source of illumination.

The specific gravities were determined at 25°C. with a calibrated two milliliter specific gravity bottle. Freshly distilled portions of the compounds were used in both the densities and refractive index determinations.

The carbon, hydrogen and nitrogen content of the β-nitrostyrenes were determined by the Rowland Chemical Laboratories with the exception of four carbon-hydrogen determinations done by the investigator. The method of Pregl was used and lead peroxide was the agent employed to trap out the oxides of nitrogen.

The properties, analyses, and yields of these new β-nitrostyrenes are summarized in Table III. Individual details not covered in the general discussion can be found in the experimental part of this section.

TABLE III

PHYSICAL CONSTANTS AND ANALYSES OF NEW β-NITROSTYRENES

Name	Formula	m.p. °C	% Yield	Calculated % N	Calculated % C	Calculated % H	Found % N	Found % C	Found % H
2-Allyloxy-β-nitrostyrene	$C_{11}H_{11}O_3N$	43-4	45.53	6.80	64.13	5.38	6.77	64.29	5.88
2-Methoxy-3-allyl-β-nitrostyrene	$C_{12}H_{13}O_3N$	54-5	19.01	6.39	65.74	5.98	6.39	65.79	5.96
4-Allyloxy-β-nitrostyrene	$C_{11}H_{11}O_3N$	90-1	67.48	6.80	64.13	5.38	6.66	64.23	5.42
3-Methoxy-4-allyloxy-β-nitrostryene	$C_{12}H_{13}O_4N$	110-11	18.71	5.95	61.27	5.58	5.84	61.18	5.55
3,4-Dimethoxy-5-allyl-β-nitrostyrene	$C_{13}H_{15}O_4N$	71-2	52.00	5.62	62.64	6.07	5.55	62.73	6.07
3-Allyloxy-β-nitrostyrene	$C_{11}H_{11}O_3N$	59-60	48.55	6.80	64.13	5.38	6.79	63.92	5.41
3-(2-Vinyloxy)ethoxy-β-nitrostyrene	$C_{12}H_{13}O_4N$	112-13	62.07	5.95	61.27	5.58	5.91	61.42	5.41
4-(2-Vinyloxy)ethoxy-β-nitrostyrene	$C_{12}H_{13}O_4N$	121-2	66.98	5.95	61.27	5.58	5.86	61.08	5.32
3-Methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene	$C_{13}H_{15}O_5N$	164-5	36.94	5.24	58.81	5.66	5.16	58.71	5.61

B. Experimental

1. Preparation of 4-Allyloxy-β-nitrostyrene

Nine and seven-tenths grams (six-hundredths mole) of 4-allyloxybenzaldehyde and three and seven-tenths grams (six-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a three hundred milliliter flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two and four-tenths grams of sodium hydroxide was dissolved in four milliliters of water, cooled to 10°C, and was added dropwise to the solution in the flask. During the addition of the sodium hydroxide a white bulky precipitate formed. The reaction was continued for an additional fifteen minutes upon completion of the addition of the base. The reaction mixture was then poured into ice water and filtered while cold into an excess of hydrochloric acid solution at a fast drop-rate with vigorous stirring. A yellow solid separated immediately which upon recrystallization gave a yield of eight and three-tenths grams.

Physical Constant: M.p. was 90-1°C.

2. Preparation of 3-Allyl-4-methoxy-β-nitrostyrene

Two attempts were made to isolate this compound according to the following methods:

a. Eight and eight-tenths grams (five-hundredths mole) of 3-allyl,4-methoxybenzaldehyde and three and one-tenth grams (five-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a three hundred milliliter flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the solution cooled to 10°C. Two grams (five-hundredths mole) of sodium hydroxide was dissolved infour milliliters of water, cooled to 10°C., and added dropwise to the contents of the flask. No precipitate formed during the addition of the base or during the additional two hours allowed for the reaction to continue. The reaction mixture was poured into ice water. A small amount of oil separated which was removed by extracting the cold solution with three twenty-milliliter portions of ether. The extracted basic solution was then added at a fast drop-rate to an excess of hydrochloric acid solution. An oil separated which was removed from the acid mixture by extracting with three twenty-milliliter portions of ether. The ether was removed under reduced pressure leaving a residue of three grams. This residue would not crystallize from several common laboratory solvents even when cooled to exceptionally low temperatures by lowering into a mixture of dry ice and acetone, nor would it freeze in the absence of solvents, thus indicating a probable freezing point well below room temperature.

b. The same procedure as in (a) was followed except that forty-five and three-tenths grams (twenty-five-hundredths mole) of 3-allyl, 4-methoxybenzaldehyde, fifteen and nine-tenths grams (twenty-five-hundredths mole) of nitromethane, and ten and four-tenths grams (twenty-five-hundredths mole) of sodium hydroxide in ten milliliters of water were used. One hundred milliliters of methanol was used as the solvent.

The residue, which remained after extracting the acid solution with four fifty-milliliter portions of ether and removal of the ether by reducing the pressure, was distilled under reduced pressure giving a yield of 6.0 grams. It was noted that a brown gas was given off during the distillation and the pressure of the system could not be lowered below three millimeters which indicated decomposition.

With the evidence of decomposition in mind, the physical constants were taken and the compound checked for nitrogen by sodium fusion. The subsequent formation of the blue precipitate of Prussian Blue indicated the presence of nitrogen. Five-tenths grams of the material was dissolved in ethanol and treated with three drops of 20% sodium methoxide in absolute ethanol. An insoluble polymer separated immediately, thus indicating the presence of the β-nitrostyrene. It became evident that the preparation of this β-nitrostyrene involves the problem of purification.

Physical Constants: D_4^{25} 1.1178; n_D^{25} 1.5452; b.p. 175-80° at 3 millimeters; MR_D calculated 61.47; MR_D found 68.56.

3. Preparation of 3-Allyloxy-β-nitrostyrene

Ten and three-tenths grams (seven-hundredths mole) of 3-allyloxybenzaldehyde and four and three-tenths grams (seven-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a three hundred milliliter flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two and eight-tenths grams of sodium hydroxide was dissolved in five milliliters of water, cooled to 10°C., and was added dropwise to the solution in the flask. No precipitate formed during the addition of the sodium hydroxide solution or in the hour following the completion of the addition. The reaction mixture was poured into ice water and the resulting solution added at a fast drop-rate to an excess of hydrochloric acid solution. A yellow precipitate formed immediately which upon recrystallization from methanol gave a yield of six and seven-tenths grams.

Physical Constant: M.p. 59-60°.

4. Preparation of 3-Methoxy-4-allyloxy-β-nitrostyrene

Nine and six-tenths grams (five-hundredths mole) of 3-methoxy-4-allyloxybenzaldehyde and three and one-tenth grams (five-hundredths

mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a three hundred milliliter flask equipped with mechanical stirrer, thermometer and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two grams (five-hundredths mole) of sodium hydroxide was dissolved in five milliliters of water, cooled to 10°C., and was added dropwise to the solution in the flask. A white, bulky precipitate formed during the addition. Fifteen minutes were allowed for the reaction to continue upon completion of the addition of the base. The reaction mixture was then poured into ice water. A white solid which separated from the aqueous solution was collected by filtration and dried. Claisen (13) reported that 3-methoxy-4-allyloxybenzaldehyde could not be distilled without effecting a small amount of rearrangement to the phenol. Recrystallization of the solid yielded a compound melting at 85-6°C. The reported melting point of 3-methoxy-4-hydroxy-5-allylbenzaldehyde was 85-6°C. The filtrate obtained when the solid was removed from the aqueous mixture, was added at a fast drop-rate to an excess of hydrochloric acid solution. A yellow, bulky precipitate formed immediately. Upon recrystallization from methanol, this precipitate gave a yield of two and two-tenths grams.

Physical Constant: M.p. 110-11°C.

5. Preparation of 3,4-Dimethoxy-5-allyl-β-nitrostyrene

Ten and two-tenths grams (five-hundredths mole) of 3,4-dimethoxy-5-allylbenzaldehyde and three and one-tenth grams (five-hundredths mole) of nitromethane were dissolved in thirty-five milliliters of methanol and placed in a flask equipped with mechanical stirrer, thermometer and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two grams (five-hundredths mole) of sodium hydroxide was dissolved in five milliliters of water, cooled to 10°C., and was added dropwise into the flask with stirring. A fine precipitate formed during the addition of the base. An additional fifteen minutes was allowed after the addition of the base for the reaction to proceed to completion. At this time the reaction mixture was poured into ice water and the resulting solution was added at a fast drop-rate to an excess of hydrochloric acid solution. A yellow, bulky precipitate began to form immediately which upon recrystallization from methanol gave a yield of six and five-tenths grams.

Physical Constant: M.p. 71-2°C.

6. Preparation of 2-(2-Vinyloxy)ethoxy-β-nitrostyrene

Two attempts were made to isolate this compound according to the following methods:

a. Nine and six-tenths grams (five-hundredths mole) of

2-(2-vinyloxy)ethoxybenzaldehyde and three and one-tenth grams (five-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two grams (five-hundredths mole) of sodium hydroxide was dissolved in five milliliters of water, cooled to 10°C., and added dropwise to the contents of the flask. No precipitate formed during the addition of the base or during the following hour allowed for the reaction to continue. The reaction mixture was poured into ice water and the resulting solution added at a fast drop-rate to an excess of hydrochloric acid solution. An oil separated from the acid solution which was collected by extracting the solution with three twenty-milliliter portions of ether. The ether was removed by reducing the pressure, leaving a residue of four and six-tenths grams. The residue would not crystallize from several common laboratory solvents, nor would it freeze in the absence of solvents when immersed in a mixture of dry ice and acetone, thus indicating a probable freezing point well below room temperature.

b. The same procedure as in (a) was followed except that forty-eight grams (twenty-five-hundredths mole) of 2-(2-vinyloxy)ethoxybenzaldehyde, fifteen and nine-tenths grams (twenty-five-hundredths mole) of nitromethane, and ten and four-tenths grams (twenty-five-

hundredths mole) of sodium hydroxide in ten milliliters of water were used. One hundred milliliters of methanol was used as the solvent.

The residue, which remained after extracting the acid solution with four fifty-milliliter portions of ether and removal of the ether, by reducing the pressure, was collected. The residue was subjected to distillation under reduced pressure. The pressure of the system could not be maintained below 1.5-2 millimeters and a brown gas was given off when the pot temperature reached 150°C. The subsequent formation of a Prussian Blue precipitate from a solution obtained by a sodium fusion, indicated the presence of nitrogen.

7. Preparation of 3-(2-Vinyloxy)ethoxy-β-nitrostyrene

Nine and six-tenths grams (five-hundredths mole) of 3-(2-vinyloxy)ethoxybenzaldehyde and three and one-tenth grams (five-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a flask equipped with mechanical stirrer, thermometer and addition funnel. The flask was placed in an ice bath and its contents lowered to 10°C. Two grams of sodium hydroxide was dissolved in four milliliters of water, cooled to 10°C., and added dropwise to the solution in the flask. The reaction was allowed to continue for fifteen minutes, following the addition of the base, and then poured into ice water. The resulting solution was added at a fast drop-rate to an excess of hydrochloric acid solution. A yellow precipitate formed immediately

which upon recrystallization from methanol gave a yield of seven and three-tenths grams.

Physical Constant: M. p. 112-13°C.

8. Preparation of 4-(2-Vinyloxy)ethoxy-β-nitrostyrene

Eight and six-tenths grams (four-hundredths mole) of 4-(2-vinyloxy)ethoxybenzaldehyde and two and five-tenths grams (four-hundredths mole) of nitromethane were dissolved in twenty-five milliliters of methanol and placed in a flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. One and six-tenths grams (four-hundredths mole) of sodium hydroxide was dissolved in four milliliters of water, cooled to 10°C., and added dropwise to the solution in the flask. A white, bulky precipitate formed during the addition of the base. The reaction was allowed to continue for fifteen minutes after completion of the addition of the base. The reaction mixture was poured into ice water and the resulting solution was added at a fast drop-rate to an excess of hydrochloric acid solution. A yellow, bulky precipitate formed which upon recrystallization from methanol gave a yield of seven and one-tenth grams.

Physical Constant: M. p. 121-2°C.

9. Preparation of 3-Methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene

Eleven and one-tenth grams (five-hundredths mole) of 3-methoxy-4-(2-vinyloxy)ethoxybenzaldehyde and three and one-tenth grams (five-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two grams (five-hundredths mole) of sodium hydroxide was dissolved in four milliliters of water, cooled to 10°C., and added dropwise to the solution in the flask. No precipitate formed during the addition of the base or during the following fifteen minutes allowed for the reaction to continue. The reaction mixture was poured into ice water and the solid separating was removed by filtration. This solid was the starting aldehyde. The filtrate was added at a fast drop-rate to an excess of hydrochloric acid solution. A yellow solid separated immediately which upon recrystallization from methanol gave a yield of four and nine-tenths grams.

Physical Constant: M.p. 164-5°C.

10. Preparation of 2-Allyloxy-β-nitrostyrene

Nine and six-tenths grams (six-hundredths mole) of 2-allyloxybenzaldehyde and three and seven-tenths grams (six-hundredths mole) of nitromethane were dissolved in thirty-five milliliters of methanol

and placed in a flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two and four-tenths grams (six-hundredths mole) of sodium hydroxide was dissolved in five milliliters of water, cooled to 10°C., and added dropwise to the contents of the flask. No bulky precipitate formed during the addition of the base. The reaction was continued for two hours. The mixture was poured into ice water and the resulting solution was added at a fast drop-rate to an excess of hydrochloric acid solution. An oil separated which was collected by extracting with three twenty-milliliter portions of ether and the ether removed by evaporation at reduced pressures. This oil was recrystallized first from methanol and then from ethanol by immersing the recrystallizing solution into a mixture of dry ice and acetone. The yield was five and five-tenths grams.

Physical Constant: M.p. 43-4°C.

11. Preparation of 2-Methoxy-3-allyl-β-nitrostyrene

Ten and five-tenths grams (six-hundredths mole) of 2-methoxy-3-allylbenzaldehyde and three and seven-tenths grams (six-hundredths mole) of nitromethane were dissolved in thirty milliliters of methanol and placed in a flask equipped with mechanical stirrer, thermometer, and addition funnel. The flask was immersed in an ice bath and the contents cooled to 10°C. Two and four-tenths grams of sodium

hydroxide was dissolved in five milliliters of water cooled to 10°C., and added dropwise to the contents of the flask. No precipitate formed during the addition of the base or in the following hour allowed for the reaction to continue. The reaction mixture was poured into ice water and the resulting solution added to an excess of hydrochloric acid solution. A yellow, bulky precipitate formed which when recrystallized first from methanol and then ethanol gave a yield of two and five-tenths grams.

Physical Constant: M.p. 54-5°C.

CHAPTER IV

POLYMERIZATION STUDIES

A. General Discussion

The polymerization studies are classified into three general groups, namely: (1) acid catalyzed polymerization, (2) base catalyzed polymerization, and (3) peroxide catalyzed polymerization. Under each of the general classifications are found one or more subgroups which include the polymerizations of the intermediate aldehydes, β-nitrostyrenes, and copolymerization of the intermediate aldehydes and the β-nitrostyrenes with maleic anhydride.

The acid catalyzed polymerizations were attempted on the β-nitrostyrenes containing the vinyloxy groups using $BF_3 \cdot (C_2H_5)_2O$ as the catalyst. Solvents which are useful in this reaction must be able to be lowered to temperatures as low as -70°C. without freezing, or precipitating the monomer to be polymerized, and showing little tendency to inhibit the polymerization reaction by competing with the monomer for the catalyst.

The aldehydes containing the vinyloxy group were polymerized with $BF_3 \cdot (C_2H_5)_2O$ when added to a solution of the catalyst and toluene at 20°C. or lower. The polymer obtained in the case of 3-(2-vinyloxy)ethoxybenzaldehyde was dissolved in nitromethane and

methanol, cooled to 10°C., and treated with sodium hydroxide solution in an effort to introduce the β-nitrostyrene grouping into the polymer.

The β-nitrostyrenes were polymerized by dissolving them in ethanol and adding a few drops of a 20% solution of sodium methoxide in absolute ethanol. The polymers formed, with the exception of two, were insoluble in ethanol. The physical characteristics of the polymers were recorded.

Each of the intermediate aldehydes and the β-nitrostyrenes obtained from them were treated with benzoyl peroxide and heated to 100°C. for twenty-four hours. The physical properties and characteristics of the materials obtained were recorded.

Each of the intermediate aldehydes and the β-nitrostyrenes were copolymerized with an equal molar quantity of maleic anhydride using benzoyl peroxide as the catalyst. The polymerization reactions were accomplished at 100°C. for twenty-four hours. The physical properties and characteristics of the material obtained were recorded.

B. Experimental

1. Acid Catalyzed Polymerizations

a. Polymerization of β-nitrostyrenes containing the vinyloxy group using $BF_3 \cdot (C_2H_5)_2O$ as the catalyst: Twenty solvents were considered for the polymerization of 3-(2-vinyloxy)ethoxy-β-nitrostyrene, 4-(2-vinyloxy)ethoxy-β-nitrostyrene and 3-methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene on the basis of solubility of the β-nitrostyrene at temperatures from 25°C. to -70°C., freezing point of the solvent, and reactivity of the solvent toward the catalyst.

No solvent was found for the polymerizations which would keep the monomers in solution when cooled to 20°C. or lower unless the ratio was one to one hundred or greater. Ten of the twenty solvents tested at room temperature would dissolve the monomers, varying in extent from very slightly soluble to infinitely soluble. These solvents were found either not to permit polymerization of a test reagent, vinyl 2-ethylhexyl ether, because of the reactivity of the $BF_3 \cdot (C_2H_5)_2O$ toward them, or to precipitate the monomeric β-nitrostyrene upon introduction of the $BF_3(C_2H_5)_2O$. Acetone and chloroform were exceptions, but it was found that the β-nitrostyrenes would not polymerize even though the vinyl 2-ethylhexyl ether would polymerize.

This lack of reactivity exhibited by the β-nitrostyrenes was further investigated because it has been shown, according to

unpublished reports by G. B. Butler, University of Florida, that vinyl phenyl ether and vinyl substituted-phenyl ethers of ethylene glycol would polymerize when treated with $BF_3 \cdot (C_2H_5)_2O$ under similar conditions as outlined above. Butler showed from the infrared spectra that, in the case of vinyl 2-methallylphenyl ether of ethylene glycol, vinyl 2-allylphenyl ether of ethylene glycol, vinyl 2-allyl-4-chlorophenyl ether of ethylene glycol, vinyl 2-crotylphenyl ether of ethylene glycol, and vinyl phenyl ether of ethylene glycol, a peak was exhibited by all of the ethers at approximately 8.34 microns. In the case of the first four named ethers, this peak disappeared completely when the polymer of each was obtained by treating the monomer with $BF_3 \cdot (C_2H_5)_2O$ as outlined above. The vinyl phenyl ether of ethylene glycol was not polymerized and checked. In the case of the vinyl 3-(2-nitrovinyl)phenyl ether of ethylene glycol, vinyl 4-(2-nitrovinyl)-phenyl ether of ethylene glycol, and vinyl 3-methoxy-4-(2-nitrovinyl)-phenyl ether of ethylene glycol, prepared by the investigator, this peak at 8.34 microns did not appear in the infrared spectra of the monomer.

Infrared spectra of the intermediate aldehydes used in preparing the β-nitrostyrenes were made. Each of the curves exhibited a peak at 8.34 microns but a check of the infrared spectra curve of benzaldehyde shows a peak at the same place. Consequently, no

definite conclusions regarding the effect of the 2-nitrovinyl group on the phenyl radical can be made on the basis of the information collected, but all known vinyl phenyl and substituted phenyl ethers of ethylene glycol have shown a tendency to polymerize under the outlined conditions with the exception of the 2-nitrovinyl substituted ones.

The solvents tested in the polymerization attempts on the β-nitrostyrenes were: diethyl ether, ethanol, methanol, ethylene dichloride, methyl chloride, carbon tetrachloride, chloroform, trichloroethylene, toluene, benzene, amyl acetate, acetone, α,α,α-trifluoro toluene, formamide, petroleum ether, b.p. 70°C., 2-propanol, 1-propanol, chlorobenzene, nitromethane, and methylene chloride.

b. Polymerization of aldehydes containing the vinyloxy group using $BF_3 \cdot (C_2H_5)_2O$ as the catalyst:

(1) Polymerization of 3-(2-vinyloxy)ethoxybenzaldehyde: A two hundred milliliter flask was fitted with a mechanical stirrer, addition funnel, calcium chloride tube filled with potassium carbonate and a low temperature thermometer. Two milliliters of dry toluene and four milliliters of $BF_3 \cdot (C_2H_5)_2O$ were placed in the flask and cooled to -35°C. by immersion of the flask in a mixture of dry ice and acetone. Five and five-tenths grams (three-hundredths mole) of 3-(2-vinyloxy)-ethoxybenzaldehyde was added dropwise over a period of one-half hour. A slight increase in temperature was noted upon the introduction

of each drop. After the addition had been completed, the reaction was allowed to continue for one hour. At the end of the reaction period, ten milliliters of methanol was introduced to inactivate the catalyst. During the polymerization reaction, solid material separated and showed little tendency to dissolve when the methanol was added. After the reaction mixture had warmed to room temperature, the insoluble material was removed by filtration. This material was white, slightly elastic, soluble in acetone, slightly soluble in methanol and softened at 85-90°C.

The toluene-methanol filtrate was distilled under reduced pressure and the residue, along with the insoluble portion collected above by filtration, was dissolved in a minimum amount of 50% methanol and nitromethane. The resulting solution was placed in a two-hundred milliliter flask equipped with mechanical stirrer, thermometer, and addition funnel. One and two-tenths grams (three-hundredths mole) of sodium hydroxide dissolved in two milliliters of water and cooled to 10°C. was added dropwise to the solution in the flask. A precipitate did not form during this addition or in the following hour allowed for the reaction to continue. Solid material precipitated upon pouring the reaction mixture into ice water. This solid material was collected by filtration and the filtrate added at a fast drop-rate with vigorous stirring to an excess of hydrochloric acid solution. The small amount

of oil present in the acid solution was extracted with two, twenty milliliter portions of ether. The volatile solvents were removed under reduced pressure and the residue, weighing two-tenths gram, was dissolved in ethanol. This ethanol solution when treated with two drops of 20% sodium methoxide in absolute ethanol showed no signs, upon heating for one hour, of polymer formation such as the formation of insoluble materials. The insoluble material obtained, when the reaction mixture was poured into ice water, was dissolved in hot ethanol and treated with two drops of a 20% solution of sodium methoxide in absolute ethanol. A precipitate did not form after heating as above.

Under these experimental conditions, it became evident that the aldehyde group in the polymer did not condense with the nitromethane in the presence of alkali, since no insoluble, amorphous materials were formed upon the introduction of sodium methoxide to solutions thought to contain β-nitrostyrene groups.

(2) Polymerization of 2-(2-vinyloxy)ethoxybenzaldehyde: One gram of 2-(2-vinyloxy)ethoxybenzaldehyde was dissolved in toluene and cooled to -30°C. One-half milliliter of $BF_3 \cdot (C_2H_5)_2O$ was added dropwise. A sharp increase in temperature was noted upon the introduction of each drop of the catalyst and the solution became very viscous. The reaction was allowed to continue for one hour. Two milliliters of methanol was added to the reaction mixture to inactivate

the catalyst. The solvent was removed by distillation under reduced pressure. The residue was very viscous, yellow in color, slightly soluble in ethanol, methanol and benzene, and soluble in acetone.

(3) Polymerization of 3-methoxy-4-(2-vinyloxy)ethoxybenzaldehyde: One gram of 3-methoxy-4-(2-vinyloxy)ethoxybenzaldehyde was dissolved in toluene and treated as in (2), except that the temperature could not be lowered below 20°C. without causing the aldehyde to crystallize. The product of the polymerization reaction was a black solid, fusing with decomposition at 115-20°C., insoluble in ethanol, methanol and benzene, and soluble in acetone.

2. Base Catalyzed Polyermizations

a. Polymerization of 4-allyloxy-β-nitrostyrene with sodium methoxide: Three-tenths gram of 4-allyloxy-β-nitrostyrene was dissolved in fifteen milliliters of absolute ethanol by heating. Upon cooling, three drops of 20% sodium methoxide in absolute ethanol was added to the solution. The solution became cloudy immediately, followed by rapid precipitation of an insoluble material. The mixture was heated for one hour on a steam bath, to insure complete reaction, cooled, and filtered to collect the solid material. After drying, the material weighed three-tenths gram, was light tan in color, fused with decomposition at 245-50°C., and was insoluble in ethanol, benzene, acetone, chloroform and methanol. The melting point of the monomer

was 90-1°C.

b. Polymerization of 3-allyloxy-β-nitrostyrene with sodium methoxide: Three-tenth grams of 3-allyloxy-β-nitrostyrene was dissolved in ten milliliters of absolute ethanol and three drops of 20% sodium methoxide in absolute ethanol was added to the solution. The solution became cloudy immediately and was heated for one hour on a steam bath to insure complete reaction. Upon cooling, the mixture gave a yield, when filtered and dried, of two-tenths gram. The material was tan in color, fused with decomposition at 235-40°C., and insoluble in ethanol, benzene, acetone, chloroform, and methanol. The melting point of the monomer was 59-60°C.

c. Polymerization of 3-methoxy-4-allyloxy-β-nitrostyrene with sodium methoxide: Three-tenths gram of 3-methoxy-4-allyloxy-β-nitrostyrene was dissolved in fifteen milliliters of ethanol and three drops of 20% sodium methoxide in absolute ethanol was added to the solution. The solution first became red and then cloudy. The resulting mixture was heated for one hour on a steam bath, cooled, the solid removed by filtration and dried. The dried material weighed two-tenths gram, was tan in color, insoluble in ethanol, benzene, acetone, chloroform and methanol but showed signs of softening in all of them. The fusion point of the material was 215-20°C. with decomposition. The melting point of the monomer was 110-11°C.

d. Polymerization of 3,4-dimethoxy-5-allyl-β-nitrostyrene with sodium methoxide: Three-tenths grams of 3,4-dimethoxy-5-allyl-β-nitrostyrene was dissolved in fifteen milliliters of absolute ethanol by heating, and upon cooling three drops of 20% sodium methoxide in absolute ethanol was added to the solution. The solution immediately became cloudy and was heated for one hour on a steam bath to insure complete reaction. Upon cooling the mixture was filtered to remove the insoluble material, which when dried gave a yield of fifteen-hundredths gram. The material was cream in color, showed no signs of fusing, but charred when heated to 360°C., was insoluble in ethanol, benzene, acetone, chloroform and methanol. The melting point of the monomer was 71-2°C.

e. Polymerization of 3-(2-vinyloxy)ethoxy-β-nitrostyrene with sodium methoxide: Three-tenths of a gram of 3-(2-vinyloxy)ethoxy-β-nitrostyrene upon warming was dissolved in twenty milliliters of ethanol and upon cooling three drops of 20% sodium methoxide in absolute ethanol were added to the solution. The solution became cloudy immediately and was heated on a steam bath for one hour to insure complete reaction. The mixture was cooled, filtered and the solid material dried. The material was brown in color, fused with decomposition at 215-20°C. and was insoluble in ethanol, benzene, acetone, chloroform and methanol. The melting point of the monomer was 112-13°C.

f. Polymerization of 4-(2-vinyloxy)ethoxy-β-nitrostyrene with sodium methoxide: Three-tenths gram of 4-(2-vinyloxy)ethoxy-β-nitrostyrene was dissolved in fifteen milliliters of ethanol by heating on a steam bath. Upon cooling, three drops of 20% sodium methoxide in absolute ethanol was added to the solution, producing a red solution followed immediately by cloudiness. The mixture was heated for one hour on a steam bath, cooled, and filtered to remove the solid material which upon drying weighed two-tenths gram.. The material was tan in color, fused with decomposition at 235-40°C., and was insoluble with signs of softening in ethanol, benzene, acetone, chloroform and methanol. The melting point of the monomer was 121-2°C.

g. Polymerization of 3-methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene with sodium methoxide: Three-tenths gram of 3-methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene upon heating was dissolved in forty-five milliliters of ethanol. Three drops of 20% sodium methoxide in absolute ethanol was added to the solution when cool, producing an immediate cloudiness. The mixture was heated for one hour on a steam bath, cooled, and filtered in order to remove the solid material. The dried material weighed twenty-five-hundredths gram, was light tan in color, fused with decomposition at 200-05°C., and was insoluble in ethanol, benzene, acetone, chloroform, and

methanol. The melting point of the monomer was 154-5°C.

h. Polymerization of 2-allyloxy-β-nitrostyrene with sodium methoxide: Three-tenths gram of 2-allyloxy-β-nitrostyrene was dissolved in ten milliliters of ethanol. The solution turned red upon addition of three drops of 20% sodium methoxide in absolute ethanol, but showed no signs of becoming cloudy even after having been heated for one hour on a steam bath. The ethanol was removed by evaporation under reduced pressure leaving a residue which failed to crystallize. This residue was slightly viscous, dark red in color, and soluble in ethanol, benzene, acetone, chloroform, and methanol. The melting point of the monomer was 43-4°C.

i. Polymerization of 2-methoxy-3-allyl-β-nitrostyrene with sodium methoxide: Three-tenths gram of 2-methoxy-3-allyl-β-nitrostyrene was dissolved in ten milliliters of ethanol and treated with three drops of 20% sodium methoxide in absolute ethanol. The solution immediately became red but showed no signs of cloudiness. The solution was heated on a steam bath for one hour without producing any insoluble material. The ethanol was evaporated under reduced pressure, leaving a dark red residue which failed to crystallize. The residue was slightly viscous, and soluble in ethanol, benzene, acetone, chloroform and methanol. The melting point of the monomer was 54-5°C.

3. Peroxide Catalyzed Polymerizations

a. Polymerization of the intermediate aldehydes with benzoyl peroxide: The following experimental procedure applies to each of the eleven aldehydes subjected to polymerization with benzoyl peroxide: five-tenths gram of the aldehyde to be polymerized along with five-hundredths gram of benzoyl peroxide were placed in a three inch test tube and mixed thoroughly. A thermometer was inserted in the test tube to observe temperature changes. The test tube was fitted with a stopper and inserted in the top of a common organic laboratory, six inch distilling column with side arm. The side arm was attached to a steam line by means of rubber tubing and the bottom of the column used to drain the condensed steam. The contents of the test tube were then heated with steam at 100°C. for twenty-four hours. Upon cooling, the physical characteristics of the material were recorded. The reaction was observed carefully at the start of the heating period for any rapid rise in temperature and any temperature increase above 100°C. which indicated polymerization.

The physical characteristics of the material obtained from each aldehyde are listed below under the name of the aldehyde used.

(1) 4-Allyloxybenzaldehyde: The temperature rose to 112°C. during the initial heating. Upon cooling, the material was very viscous and tacky, soluble in acetone and chloroform, and insoluble in

benzene, toluene, ethanol, and methanol. The color of the final material was red as compared to pale yellow for the monomer.

(2) 3-Allyl-4-methoxybenzaldehyde: A temperature increase was not noted during the initial heating. Upon cooling, the material was slightly viscous, soluble in benzene, toluene, chloroform, and acetone, and insoluble in ethanol and methanol. The color of the final material was red as compared to yellow for the monomer.

(3) 3-Allyloxybenzaldehyde: A temperature increase was not noted during the initial heating. Upon cooling, the material was viscous, soluble in acetone, benzene, toluene, and chloroform, and insoluble in ethanol and methanol. The color of the final material was red as compared to white for the monomer.

(4) 3-Methoxy-4-allyloxybenzaldehyde: A temperature increase was not noted during the initial heating. Upon cooling, the material was not viscous and soluble in acetone, benzene, toluene, chloroform, ethanol, and methanol. The color of the final material was red as compared to pale yellow for the monomer.

(5) 3,4-Dimethoxy-5-allylbenzaldehyde: A temperature increase was not noted during the initial heating. Upon cooling, the material was very slightly viscous, soluble in benzene, toluene, chloroform, acetone, and insoluble in ethanol and methanol. The color of the final material was red as compared to yellow for the monomer.

(6) 2-(2-Vinyloxy)ethoxybenzaldehyde: The temperature increased to 110°C during the initial heating. Upon cooling, the material was very viscous, soluble in benzene, toluene, chloroform, acetone, nitromethane, and insoluble in ethanol and methanol. The final material was pale yellow in color.

(7) 3-(2-Vinyloxy)ethoxybenzaldehyde: The temperature increased to 107°C. during the initial heating. Upon cooling, the material was viscous, soluble in benzene, toluene, chloroform, acetone, and nitromethane and insoluble in ethanol and methanol. The final material was yellow in color.

(8) 4-(2-Vinyloxy)ethoxybenzaldehyde: The temperature increased to 145°C. during the initial heating. Upon cooling, the material was very viscous, slightly soluble in benzene, and toluene, soluble in chloroform, acetone and nitromethane, and insoluble in ethanol and methanol. The color of the final material was yellow.

(9) 3-Methoxy-4-(2-vinyloxy) ethoxybenzaldehyde: The temperature increased to 125°C. during the initial heating. Upon cooling, the material became glassy. The material was soluble in benzene, toluene, chloroform, acetone, and nitromethane, insoluble in ethanol and methanol and fused at 60-5°C. The color of the final material was red.

(10) 2-Allyloxybenzaldehyde: A temperature increase was not

noted during the initial heating. Upon cooling, the material was not viscous, was soluble in benzene, toluene, chloroform, acetone, and slightly soluble in ethanol and methanol. The final material was red in color as compared to yellow for the original monomer.

(11) 2-Methoxy-3-allylbenzaldehyde: A temperature increase was not noted during the initial heating. Upon cooling, the material was not viscous and was soluble in benzene, toluene, chloroform, acetone, methanol, and ethanol. The color of the final material was red as compared to yellow for the monomer.

b. Copolymerization of the intermediate aldehydes and maleic anhydride with benzoyl peroxide: The following experimental procedure applies to the copolymerization of each aldehyde and maleic anhydride with benzoyl peroxide: five-tenths gram of the aldehyde, twenty-five-hundredths gram of maleic anhydride, and five-hundredths gram of benzoyl peroxide were placed in a three inch test tube and mixed thoroughly. A thermometer was inserted in the test tube to observe temperature changes. The test tube was fitted with a stopper and inserted in the top of a common organic laboratory, six inch distilling column with side arm. The side arm was attached to a steam line by means of rubber tubing and the bottom of the column used to drain the condensed steam. The contents of the test tube were then heated with steam at 100°C. for twenty-four hours. Upon cooling, the

physical characteristics of the material were recorded. The reaction was observed carefully at the start of the heating period for any rapid rise in temperature and any temperature increase above 100°C. which would indicate polymerization.

The physical characteristics of the material obtained from each aldehyde are listed below under the name of the aldehyde used.

(1) 4-Allyloxybenzaldehyde: The temperature increased to 158°C. during the initial heating. Upon cooling, the material was very viscous, almost a glass, red in color, slightly soluble in acetone, and dilute base, and insoluble in benzene, toluene, methanol, ethanol, and chloroform.

(2) 3-Allyl-4-methoxybenzaldehyde: The temperature increased to 125°C. during the initial heating. Upon cooling, the material was a glass, red in color, fused at 45-50°C., was soluble in acetone, slightly soluble in benzene, toluene, chloroform, and insoluble in ethanol and methanol.

(3) 3-Allyloxybenzaldehyde: The temperature increased to 135°C. during the initial heating. Upon cooling, the material was a glass, red in color, fused at 60-65°C., was soluble in acetone, base, slightly soluble in chloroform, and insoluble in benzene, toluene, methanol, and ethanol.

(4) 3-Methoxy-4-allyloxybenzaldehyde: A temperature increase

was not noted during the in itial heating. Upon cooling, the material showed no signs of polymerization but had changed from yellow to red in color. The final material was soluble in benzene, toluene, chloroform, acetone, ethanol, and methanol.

(5) 3,4-Dimethoxy-5-allylbenzaldehyde: The temperature increased to 110°C. during the initial heating. Upon cooling, the material was viscous, red in color, soluble in acetone, base, and chloroform, slightly soluble in benzene and toluene, and very slightly soluble in ethanol and methanol.

(6) 2-(2-Vinyloxy)ethoxybenzaldehyde: The temperature increased to 130°C. during the initial heating. Upon cooling, the material was a glass, softening at 110-15°C., red in color, soluble in base, insoluble in benzene, toluene, chloroform, methanol, ethanol, and acetone.

(7) 3-(2-Vinyloxy) ethoxybenzaldehyde: The temperature increased to 136°C. during the initial heating. Upon cooling, the material was a glass, yellow in color, softening at 60-65°C., was soluble in base and insoluble in benzene, toluene, chloroform, acetone, ethanol, and methanol.

(8) 3-Methoxy-4-(2-vinyloxy)ethoxybenzaldehyde: The temperature increased to 149°C. during the initial heating. Upon cooling, the material was a glass, dark brown in color, softened at 115-20°C.

with decomposition, was soluble in base and acetone, slightly soluble in chloroform, and insoluble in benzene, toluene, methanol, and ethanol.

(9) 2-Allyloxybenzaldehyde: The temperature increased to 131°C. during the initial heating.. Upon cooling, the material was very viscous, red in color, soluble in acetone and base, very slightly soluble in benzene and toluene, and insoluble in methanol and ethanol.

(10) 2-Methoxy-3-allylbenzaldehyde: The temperature increased to 134°C. during the initial heating. Upon cooling, the material was viscous, dark brown in color, soluble in base, acetone, and chloroform, slightly soluble in benzene and toluene, and very slightly soluble in ethanol and methanol.

c. Polymerization of the β-nitrostyrenes with benzoyl peroxide: The following experimental procedure applies to each of the nine β-nitrostyrenes subjected to polymerization with benzoyl peroxide: five-tenths gram of the β-nitrostyrene and five-hundredths gram of benzoyl peroxide were placed in a three inch test tube and mixed thoroughly. A thermometer was inserted in the test tube to observe temperature changes. The test tube was fitted with a stopper and inserted in the top of a common organic laboratory, six-inch distilling column with side arm. The side arm was attached to a steam line by means of rubber tubing and the bottom of the column used to drain the condensed steam.

The contents of the test tube were then heated with steam at 100°C. for twenty-four hours. Upon cooling, the physical characteristics of the material were recorded. The reaction was observed carefully at the start of the heating period for any rapid rise in temperature and any temperature increase above 100°C. which indicated polymerization.

The physical characteristics of the material obtained from each β-nitrostyrene are listed below under the name of the β-nitrostyrene used.

(1) 4-Allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The material upon cooling was viscous, dark brown in color, would not crystallize from methanol, was soluble in acetone, and very slightly soluble in benzene, chloroform and toluene. The melting point of the original monomer was 90-1°C.

(2) 3-Allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The material upon cooling was viscous, dark red in color, would not crystallize from methanol, was soluble in acetone, and insoluble in benzene, toluene and chloroform. The melting point of the original monomer was 59-60°C.

(3) 3-Methoxy-4-allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Upon cooling, the material was recrystallized from methanol. The melting point of the material recovered was 107-09°C. The melting point of the original

monomer was 110-11°C. No change was observed in a mixed melting point.

(4) 3,4-Dimethoxy-5-allyl-β-nitrostyrene: A temperature increase was not noted during the initial heating. Upon recrystallization from methanol, a compound melting at 68-70°C. was recovered. The melting point of the original monomer was 71-2°C. A mixed melting point showed no deflection.

(5) 3-(2-Vinyloxy)ethoxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The material upon cooling was viscous, dark brown in color, would not recrystallize from methanol, was soluble in acetone, slightly soluble in chloroform and very slightly soluble in benzene and toluene. The melting point of the original monomer was 112-13°C.

(6) 4-(2-Vinyloxy)ethoxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The material upon cooling was viscous, black in color, would not recrystallize from methanol, was soluble in acetone, and slightly soluble in chloroform, benzene, and toluene. The melting point of the original monomer was 121-2°C.

(7) 3-Methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The material upon cooling was viscous, dark red in color, would not recrystallize

from methanol, was soluble in acetone, and insoluble in chloroform, benzene, and toluene. The melting point of the original monomer was 164-5°C.

(8) 2-Allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The material upon cooling was viscous, brown in color, would not recrystallize from methanol, was soluble in acetone, and insoluble in benzene, chloroform, and toluene. The melting point of the original monomer was 43-4°C.

(9) 2-Methoxy-3-allyl-β-nitrostyrene: A temperature increase was not noted. The material upon cooling was slightly viscous, dark red in color, would not recrystallize from methanol, was soluble in acetone, and slightly soluble in benzene, chloroform and toluene. The melting point of the original monomer was 54-5°C.

d. Copolymerization of the β-nitrostyrenes and maleic anhydride with benzoyl peroxide: The following experimental procedure applies to the copolymerization of each β-nitrostyrene and maleic anhydride with benzoyl peroxide: five-tenths gram of the β-nitrostyrene, twenty-five-hundredths gram of maleic anhydride, and five-hundredths gram of benzoyl peroxide were placed in a three inch test tube and mixed thoroughly. A thermometer was inserted in the test tube to observe temperature changes. The test tube was fitted with a stopper and inserted in the top of a common organic laboratory six inch distilling

column with side arm. The side arm was attached to a steam line by means of rubber rubing and the bottom of the column used to drain the condensed steam. The contents of the test tube were then heated at 100°C. for twenty-four hours. Upon cooling, the polymerization mixture was extracted with benzene to remove any maleic anhydride which remained unreacted. The benzene insoluble material was checked to determine if it were the original β-nitrostyrene or a polymer. The insoluble material, which did not correspond to the original β-nitrostyrene, was examined and its physical characteristics recorded. The polymerization reaction was observed carefully at the start of the heating period for any rapid rise in temperature and any temperature increase above 100°C. which would indicate polymerization.

(1) 4-Allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the cooled material with benzene, yielded three-tenths gram of product, fusing with decomposition at 110-15°C., brown in color, soluble in base, very slightly soluble in acetone and insoluble in benzene, toluene, methanol, ethanol, and chloroform. The melting point of the original monomer was 90-1°C.

(2) 3-Allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the cooled material with benzene, yielded three-tenths gram of product fusing with decomposition at 90-110°C., brown in color, soluble in acetone and base, and

insoluble in ethanol, methanol, chloroform and toluene. The melting point of the original monomer was 59-60°C.

(3) 3-Methoxy-4-allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Recrystallization of the polymerization reaction mixture produced three-tenths gram of material melting at 108-110°C. The melting point of the original monomer was 110-11°C. No change in a mixed melting point was observed.

(4) 3,4-Dimethoxy-5-allyl-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the cooled material with benzene, yielded four-tenths gram of material fusing with decomposition at 105-110°C., dark red in color, soluble in acetone and base, insoluble in ethanol, methanol, chloroform, and toluene. The melting point of the original monomer was 71-2°C.

(5) 3-(2-Vinyloxy)ethoxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. The dark brown, viscous material obtained upon cooling, was soluble in base and acetone, slightly soluble in methanol, and insoluble in ethanol, benzene, toluene, and chloroform. The melting point of the original monomer was 112-13°C.

(6) 4-(2-Vinyloxy)ethoxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the

viscous brown material with benzene did not yield a solid. Evaporation of the benzene extract did not produce a trace of maleic anhydride. The viscous material was soluble in base, acetone, slightly soluble in chloroform, and insoluble in methanol, ethanol, benzene, and toluene. The melting point of the original monomer was 121-2°C.

(7) 3-Methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the cooled material with benzene yielded a dark brown material, fusing at 205-10°C., soluble in base and acetone, and insoluble in toluene, chloroform, ethanol, and methanol. The melting point of the original monomer was 164-5°C.

(8) 2-Allyloxy-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the cooled material with benzene yielded three-tenths gram of dark brown material, fusing at 60-5°C., soluble in base and acetone, very slightly soluble in toluene and chloroform, and insoluble in methanol and ethanol. The melting point of the original monomer was 43-4°C.

(9) 2-Methoxy-3-allyl-β-nitrostyrene: A temperature increase was not noted during the initial heating. Extraction of the cooled material, with benzene, yielded four-tenths gram of a light tan solid, fusing at 155-60°C., soluble in base and acetone, slightly soluble in chloroform, and insoluble in ethanol, methanol, and toluene. The

melting point of the original monomer was 54-5°C.

CHAPTER V

DISCUSSION OF RESULTS

Condensation of phenols containing the aldehyde group with allyl bromide and vinyl 2-chloroethyl ether was accomplished in the majority of the cases with ease and in good yields. Instead of refluxing the mixture composed of the phenol, the halogenated compound, potassium carbonate, and the solvent, absolute ethanol, the halogenated compound was added to a solution of the phenol in sodium hydroxide and then refluxed. The time necessary for the condensation to take place varied. The less reactive vinyl 2-chloroethyl ether required twenty-four hours of heating as compared to approximately five hours for the condensation of allyl bromide.

The rearranged allyl ethers were not isolated but were dissolved in a solution of sodium hydroxide and condensed with dimethyl sulfate under conditions very similar to the previously outlined condensation of allyl bromide with the phenol.

Altogether, eleven aldehydes were prepared by the methods listed above. Seven of the aldehydes have not been reported previously in the literature. No attempt was made to prepare derivatives of the new aldehydes other than the β-nitrostyrene. Physical constants were determined and analyses made on the new aldehydes.

The method of Worrall (61) was used to convert nine of the eleven aldehydes prepared into the β-nitrostyrenes. The yields obtained varied from 18.7 to 66.9 per cent. Two of the aldehydes, namely 3-allyl-4-methoxybenzaldehyde and 2-(2-vinyloxy)ethoxybenzaldehyde, condensed with nitromethane, but their β-nitrostyrenes were not obtained in a form pure enough to determine their physical constants or for analyses. Several unsuccessful attempts were made to crystallize the impure β-nitrostyrenes from various solvents. Decomposition of the β-nitrostyrenes resulted when they were subjected to distillation. It was evident that purification and not the method of preparation of the two β-nitrostyrenes was the factor to overcome.

The two stage polymerization of the β-nitrostyrenes, as outlined in the Statement of the Problem, was studied and found under the conditions used in this investigation to be impractical if not impossible.

Polymerization of the β-nitrostyrenes in ethanol with sodium methoxide produced insoluble polymers in all cases with the exception of the two β-nitrostyrenes which were ortho substituted. Even though it was known that β-nitrostyrene itself and substituted β-nitrostyrenes produced insoluble polymers, it was desirable to determine whether or not the same was true for the β-nitrostyrenes prepared during this investigation. Since the polymers obtained are insoluble, or fuse at temperatures of 200° or higher, it became impossible to cross-link

the polymers by using other catalysts such as peroxides for the polymers of β-nitrostyrenes containing allyl or allyloxy groups and $BF_3 \cdot (C_2H_5)_2O$ for the polymers of β-nitrostyrenes containing the vinyloxy group.

It is possible in the case of the two ortho substituted β-nitrostyrenes, namely, 2-allyloxy-β-nitrostyrene and 2-methoxy-3-allyl-β-nitrostyrene, which, when treated with sodium methoxide, did not produce insoluble polymers, that sterically the polymerization was inhibited, thus producing very low molecular weight polymers which would show considerable differences in solubility. None of the original monomer could be recovered from the material obtained in the case of the ortho substituted β-nitrostyrenes.

Polymerization of the β-nitrostyrenes containing the vinyloxy group, namely 3-(2-vinyloxy)ethoxy-β-nitrostyrene, 4-(2-vinyloxy)-ethoxy-β-nitrostyrene, and 3-methoxy-4-(2-vinyloxy)ethoxy-β-nitrostyrene, with $BF_3 \cdot (C_2H_5)_2O$ in an effort to produce linear polymers, which would lend themselves to cross-linking through the 2-nitrovinyl group, was not only complicated by the fact that solvents could not easily be found to support the reaction, but, when they were found, no evidence of polymerization was obtained. A test reagent, vinyl 2-ethylhexyl ether, polymerized under the same conditions.

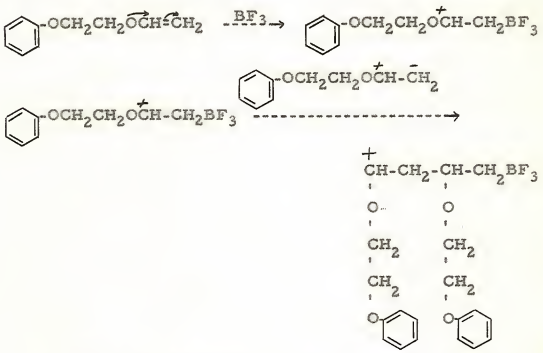
According to unpublished information obtained from G. B. Butler, University of Florida, vinyl phenyl ether and vinyl substituted-phenyl

ethers of ethylene glycol have been polymerized when treated with $BF_3 \cdot (C_2H_5)_2O$ under the conditions employed in the case of the β-nitrostyrene derivatives. Butler also showed by infrared spectra that, in the case of vinyl 2-methallylphenyl ether of ethylene glycol, vinyl 2-allylphenyl ether of ethylene glycol, vinyl 2-allyl-4-chlorophenyl ether of ethylene glycol, vinyl 2-crotylphenyl ether of ethylene glycol, and vinyl phenyl ether of ethylene glycol, a peak was exhibited by all of the ethers at approximately 8.34 microns. This peak, in the case of the first four named ethers, disappeared completely when the polymer of each obtained by treating the monomer with $BF_3 \cdot (C_2H_5)_2O$, as previously described, was checked by infrared. Vinyl phenyl ether of ethylene glycol was not polymerized and checked. In the case of the three previously mentioned β-nitrostyrenes, this peak at 8.34 microns did not appear in the infrared spectra of the monomer.

Since vinyl phenyl and all known vinyl substituted-phenyl ethers of ethylene glycol, including the ones prepared in this investigation have shown a tendency to polymerize under the outlined conditions with the exception of the discussed β-nitrostyrenes, it becomes apparent that the 2-nitrovinyl group plays a definite role in preventing the polymerization of the β-nitrostyrenes containing the vinyloxy group.

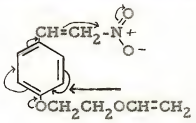
Polymerization of any vinyl or vinyl substituted-phenyl ether with $BF_3 \cdot (C_2H_5)_2O$ would involve the attaching of the BF_3 to the

terminal carbon atom of the vinyloxy group. This would be accomplished when a pair of the electrons making up part of the double bond shifts to the terminal carbon atom, thus producing one of its possible resonance structures. The attachment of the BF_3 to this negative carbon atom would destroy the resonance, thus leaving a positive carbon atom. This positive carbon atom would attach itself to a negative carbon atom in the same manner as BF_3. Such a process would eventually produce a long chain molecule. The mechanism of the reaction is illustrated by the following equation:



It is apparent that anything preventing or inhibiting the initial shift of the pair of electrons making up the double bond also prevents the possibility of the polymerization of the compound with acid type

catalysts such as $BF_3 \cdot (C_2H_5)_2O$. On the basis of the absence of a peak of 8.34 microns, which was considered to be due to the actual shifting of the electrons in the vinyloxy group, this preventing or inhibiting of the electron shift appears to be the reason why polymers were not obtained from the β-nitrostyrenes under consideration. An examination of the structure of the β-nitrostyrenes showed that the resonance and inductive effects could inhibit, if not completely prevent, any shift of electrons necessary to promote polymerization. The following structure illustrates the discussed effects:



The lack of reactivity of the vinyloxy group toward polymerization with $BF_3 \cdot (C_2H_5)_2O$ in the β-nitrostyrenes prevented the formation of linear polymers capable of being cross-linked through the 2-nitrovinyl group with sodium methoxide. This lack of reactivity would be expected in the intermediate aldehydes, but to a lesser degree than would be found in the β-nitrostyrenes. Since the aldehydes were polymerized with $BF_3 \cdot (C_2H_5)_2O$, it became evident that the aldehyde group does not have as great an inhibiting effect as the 2-nitrovinyl group, even though the same type of resonance and inductive effect is

possible.

The linear polymer of 3-(2-vinyloxy)ethoxybenzaldehyde obtained by using $BF_3 \cdot (C_2H_5)_2O$ as the catalyst, was dissolved in nitromethane and methanol, followed by the addition of sodium hydroxide in an effort to introduce the 2-nitrovinyl group into the polymer. Under the conditions of the experiment, no evidence of condensation of the nitromethane and aldehyde group was found.

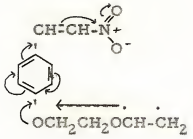
Polymerization reactions of the aldehydes and β-nitrostyrenes singly, and copolymerization of each aldehyde and β-nitrostyrene individually, with maleic anhydride using benzoyl peroxide as the catalyst, were studied. The aldehydes in all cases showed a greater tendency to polymerize than did their analogous β-nitrostyrenes.

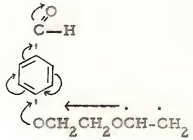
The failure of 3-methoxy-4-allyloxybenzaldehyde and 3-methoxy-4-allyloxy-β-nitrostyrene to copolymerize individually with maleic anhydride, using benzoyl peroxide as the catalyst, can possibly be attributed to the presence of a trace of 3-methoxy-4-hydroxy-5-allylbenzaldehyde, which formed in the preparation of 3-methoxy-4-allyloxybenzaldehyde. Phenols are known to inhibit peroxide catalyzed polymerizations.

The normally ready response of monovinyl ethers to electrophilic catalysts and their comparatively low reactivity in free radical polymerizations have been attributed to their electron-rich double

bond and to a low degree of resonance. Due to this low reactivity, it has been incorrectly stated that vinyl alkyl ethers do not homopolymerize in aqueous emulsion because they are so readily hydrolyzed. Actually, vinyl alkyl ethers, such as the isobutyl monomer, very slowly yield viscous liquid low polymers under the action of lauroyl peroxide in bulk at 60°C., by alkaline persulfate emulsion, as well as by the action of ultraviolet light. Only by ionic polymerization have high-molecular, solid homopolymers been obtained from the lower alkyl vinyl ethers (52).

It is theoretically possible that the tendency of the aldehydes and β-nitrostyrenes containing the vinyloxy group to polymerize singly and copolymerize individually with maleic anhydride, when treated with benzoyl peroxide, was accomplished because of the possible resonance and inductive effects. The tendency of free-radical formation, based on the electrophilic nature of the ring substitution, would be greater in the case of the aldehyde. The electrons making up the double bond in the vinyloxy group would not shift to the terminal carbon atom as readily when electrophilic groups were ring-substituted thus making it possible for the electrons to shift and form free radicals, which would lend themselves to a greater extent to polymerization under the influence of peroxide catalysts. The following structures illustrate the discussed effects:





Experimental evidence showed that, in all cases, the aldehydes containing the vinyloxy group polymerized singly and copolymerized individually with maleic anhydride, using benzoyl peroxide as the catalyst. The polymers obtained were very viscous with the exception of one which was a glass.

None of the β-nitrostyrenes containing the vinyloxy group showed the tendency to polymerize as readily as their analogous aldehydes under the same conditions.

CHAPTER VI

SUMMARY

Eleven aldehydes were prepared, seven of which were not reported previously in the literature. Physical constants were determined and analysis made for each new aldehyde. The aldehydes were prepared by reacting the appropriate hydroxybenzaldehyde in a solution of sodium hydroxide with allyl bromide, rearrangement of the product obtained, and condensation of the resulting hydroxy-allyl-substituted benzaldehyde in a solution of sodium hydroxide with dimethyl sulfate.

Nine new β-nitrostyrenes were obtained from the aldehydes prepared. Two of the aldehydes apparently formed the β-nitrostyrenes but could not be purified sufficiently to permit characterization. Physical constants were determined and analysis made for each new β-nitrostyrene. The β-nitrostyrenes were prepared by condensing the appropriate aldehyde with nitromethane in the presence of sodium hydroxide. The salt formed during this condensation was converted to the β-nitrostyrene by adding it as an aqueous solution to an excess of hydrochloric acid solution.

The β-nitrostyrenes were subjected to polymerization with sodium methoxide. Only the β-nitrostyrenes which were ortho

substituted with regards to the 2-nitrovinyl group failed to produce insoluble polymers.

The β-nitrostyrenes and aldehydes containing the vinyloxy group were subjected to polymerization using $BF_3 \cdot (C_2H_5)_2O$ as the catalyst. The aldehydes polymerized but the β-nitrostyrenes were recovered as the monomer from the reaction solution. Infrared evidence pointed to an inhibition or prevention of the electron shift in the vinyloxy group which was necessary to permit polymerization.

The aldehydes and β-nitrostyrenes were polymerized singly, and copolymerized individually, with maleic anhydride using benzoyl peroxide as the catalyst. The aldehyde in all cases showed a greater tendency to polymerize than did its analogous β-nitrostyrene derivative.

The two-stage polymerizations which were proposed originally, were not practical because of the lack of solubility of the polymers obtained with sodium methoxide, the lack of reactivity of the vinyloxy group in the β-nitrostyrenes toward BF_3 and the slight tendency of the β-nitrostyrenes to polymerize with benzoyl peroxide.

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James L. Nash, Jr. was born in Muhlenberg County, Kentucky, on September 24, 1926. He pursued his undergraduate studies at Western Kentucky State College, Bowling Green, Kentucky, and was awarded the degree of Bachelor of Science in August, 1948.

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COMMITTEE REPORT

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of the committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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